



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Analytical Approaches Towards Understanding Structure-Property Relationships in End-Linked Model PDMS Networks

J. P. Lewicki , R. L. F. Albo, C. T. Alviso, M.
Ashmore, S. J. Harley, J. A. Finnie, R. S. Maxwell

September 4, 2012

MODEST 2012
Prauge, Czech Republic
September 2, 2012 through September 7, 2012

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Analytical Approaches Towards Understanding Structure-Property Relationships in End-Linked Model PDMS Networks

James P. Lewicki, Rebecca L. F. Albo, Cynthia T. Alviso,
Jasmine Finnie, Stephen J. Harley, Michael Ashmore and
Robert S. Maxwell



LLNL-PRES-XXXXXX

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC



Siloxane Based Engineering Materials – Complex Materials with Complex Aging Behaviors

Structural complexity over a range of size-scales

Complex engineering
silicones

Bulk

Network
structure

Chemical
identity



LOAD

-H₂O

$\alpha\beta\gamma$

Δ

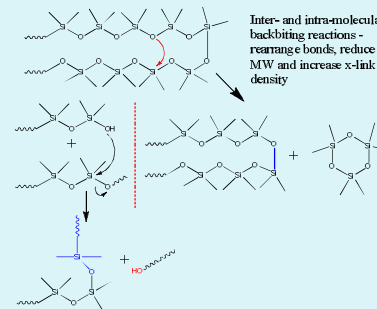
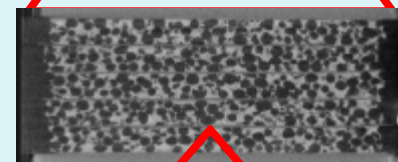
**Aging and
degradation
mechanisms
operate over a
broad range of
size scales**

Macro

Micro

Molecular

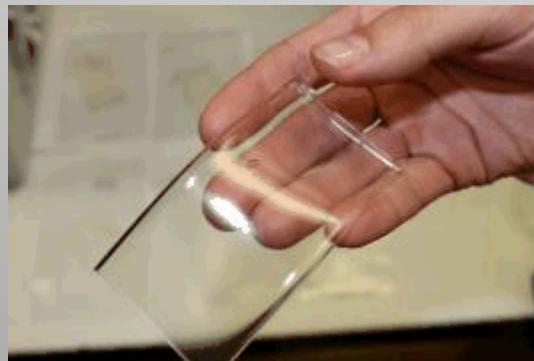
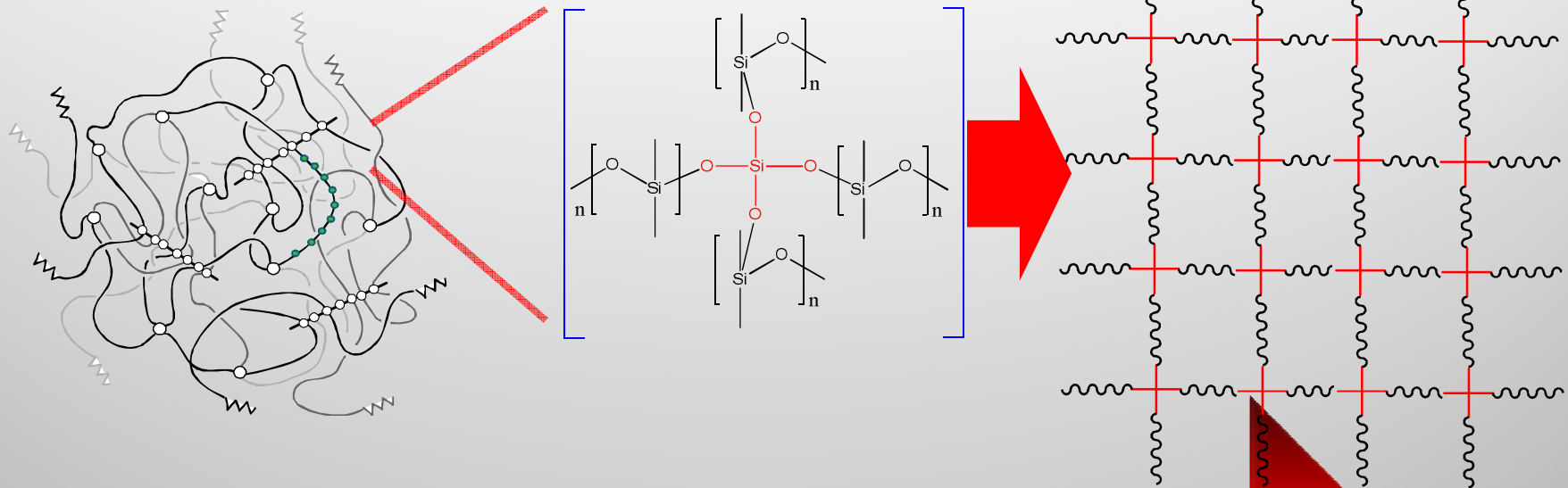
Suffer aging and
degradation



Aging and degradation over a range of size-scales

Building Model Networks to Study Aging and Degradation

By reproducing basic structural motifs individually, we can synthesize practical physical model networks.



Pyrolysis-Gas Chromatography/Mass Spectrometry

Interrogative thermal analysis of siloxane network architecture

Probe head

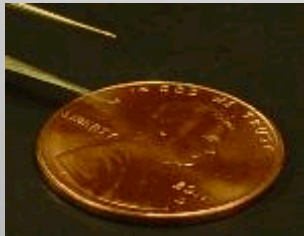
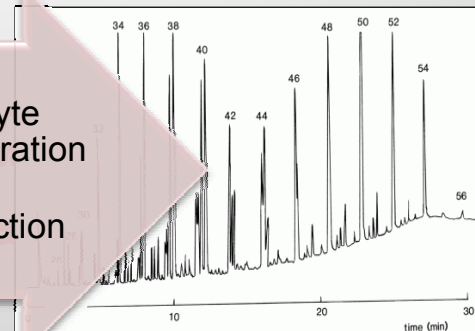
- Sample
- He carrier gas

Furnace

- Δ
- Analytes evolved

GCMS

- Analyte separation
- MS detection



Small sample size
(0.05mg):

- *Non-diffusion limited regime*



Versatile probe designs:

- *'low & slow' out-gassing*
- *thermal degradation*



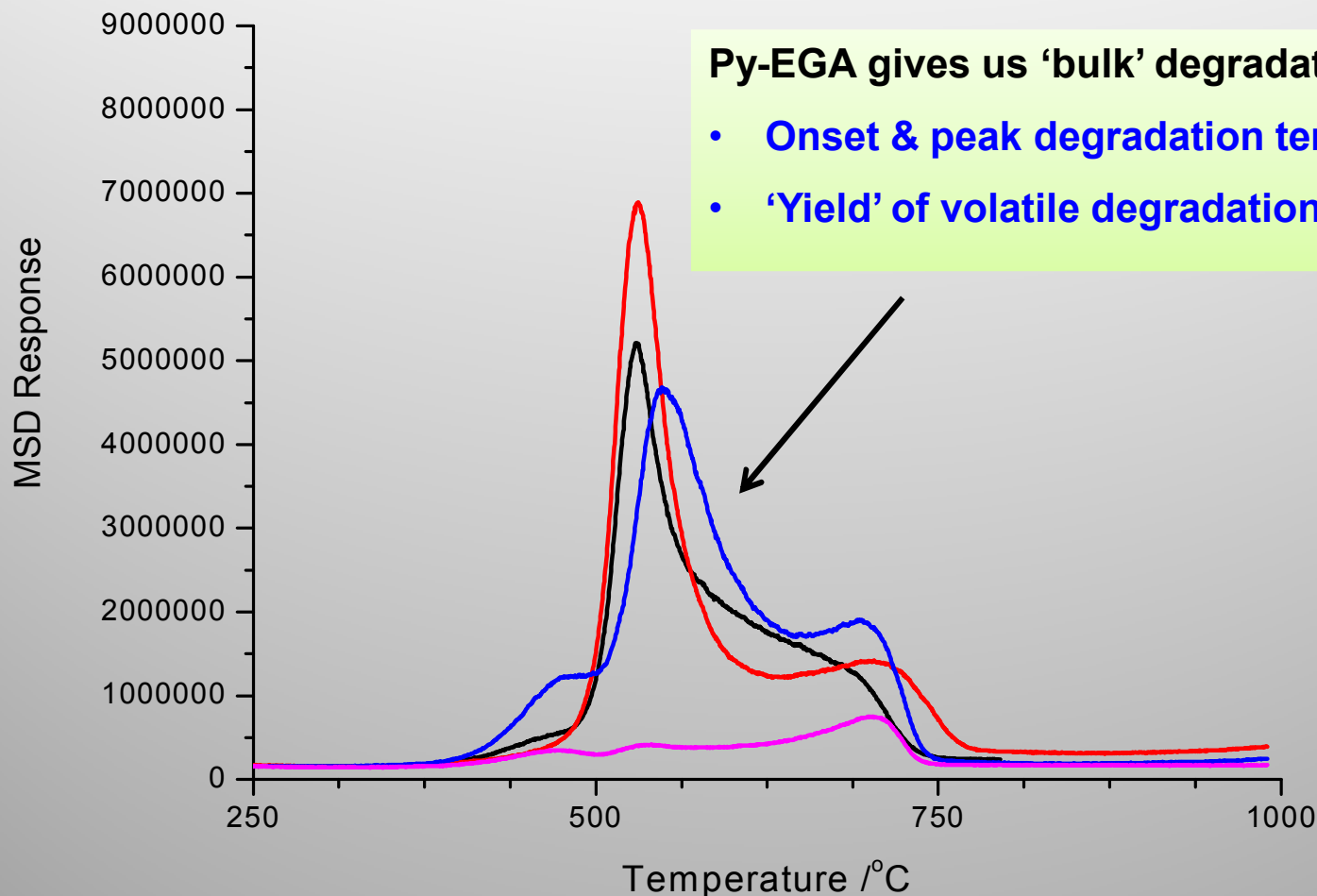
Cryo-GC/MS:

- *High sensitivity*
- *Efficient separation*
- *broad mass detection*

What Information can Py-GCMS provide?

Pyrolysis-evolved gas analysis (Py-EGA)

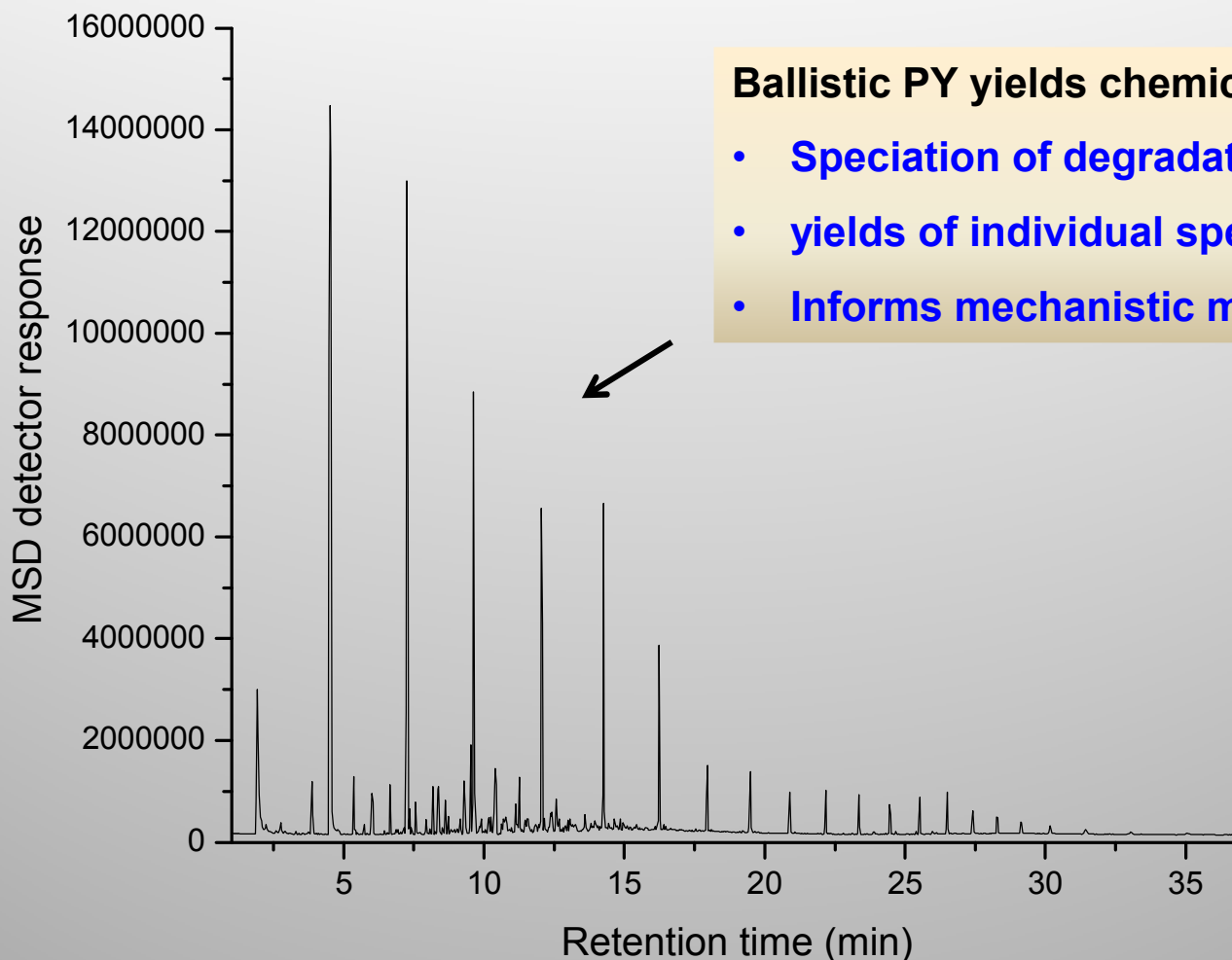
(20 °C/min) with GC column in a non-eluting mode, Carbon NT/PDMS composites



What Information can Py-GCMS provide?

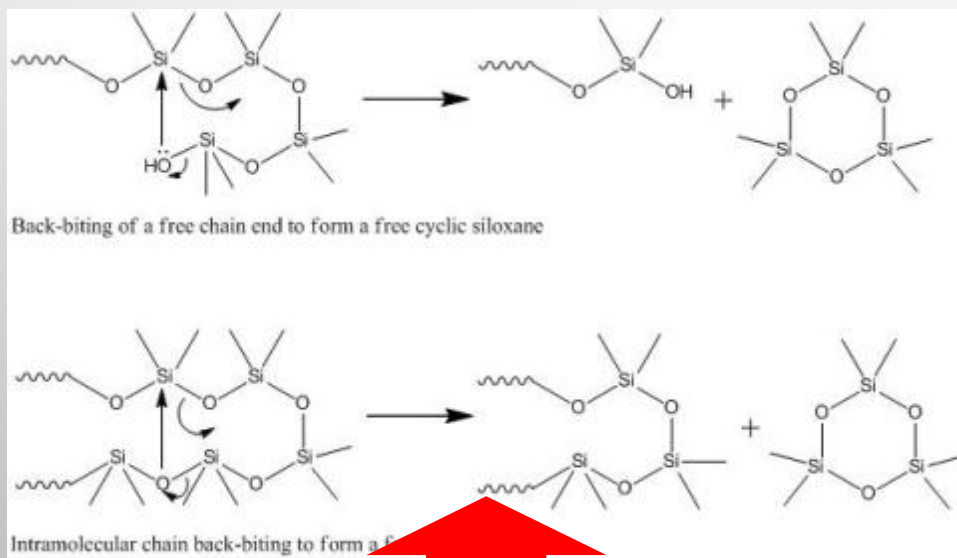
Ballistic pyrolytic analysis

(1000 °C/min) with GC column in an eluting mode



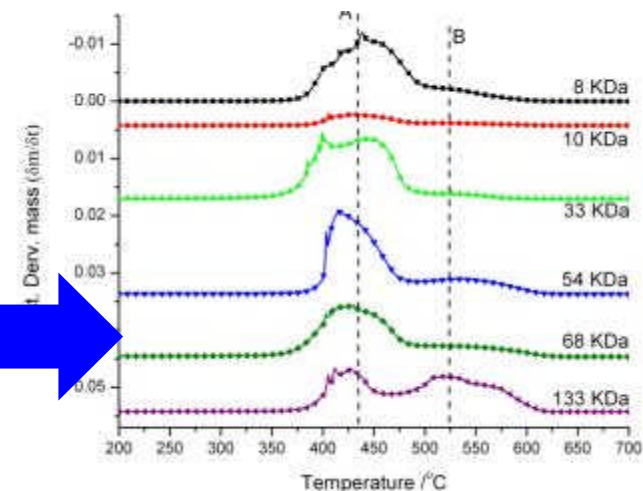
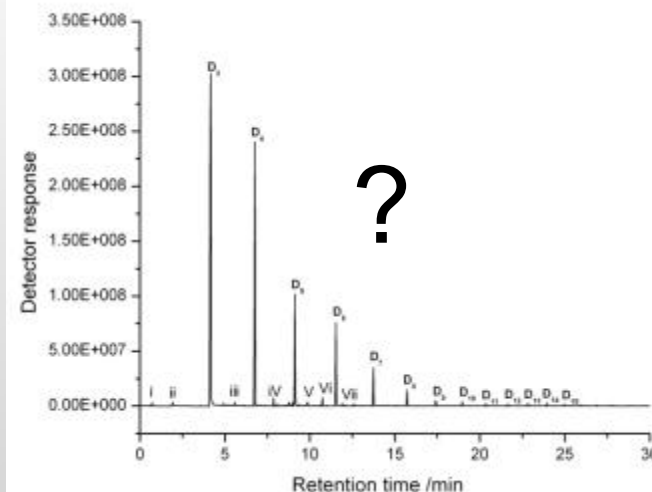
Thermal Degradation in Siloxane Networks

Does network structure influence degradation chemistry?



- Siloxanes thermally degrade via well established chemistries to form a series of cyclic oligomers
- We've shown that network structure can influence the stability of a PDMS network in the bulk*.

1) Lewicki JP, Mayer, BP, Alviso CT, and Maxwell, RS." *Journal of Inorganic and Organometallic Polymers and Materials* (2012) 22:636–645).

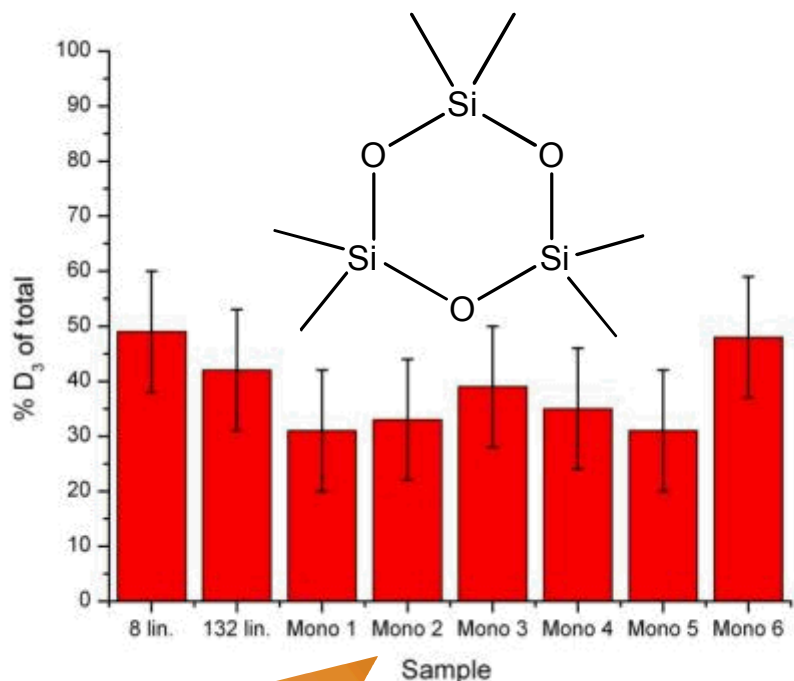


Analytical Thermal Analysis of Siloxane Networks

How does the network structure affect the mechanisms of degradation?

Studied Architectures:

- *Mono-modal*
- *Bi-Modal*
- *Free-chain end systems*
- *Above and below entanglement*
- *(liquid precursors)*



Using Quantitative GC-Pyrolysis we have shown that the D₃ cyclic remains the principle product of degradation, irrespective of network structure^{1,2}

1 Lewicki JP, Mayer, BP, Alviso CT, and Maxwell, RS." *Journal of Inorganic and Organometallic Polymers and Materials* (2012) 22:636–645).

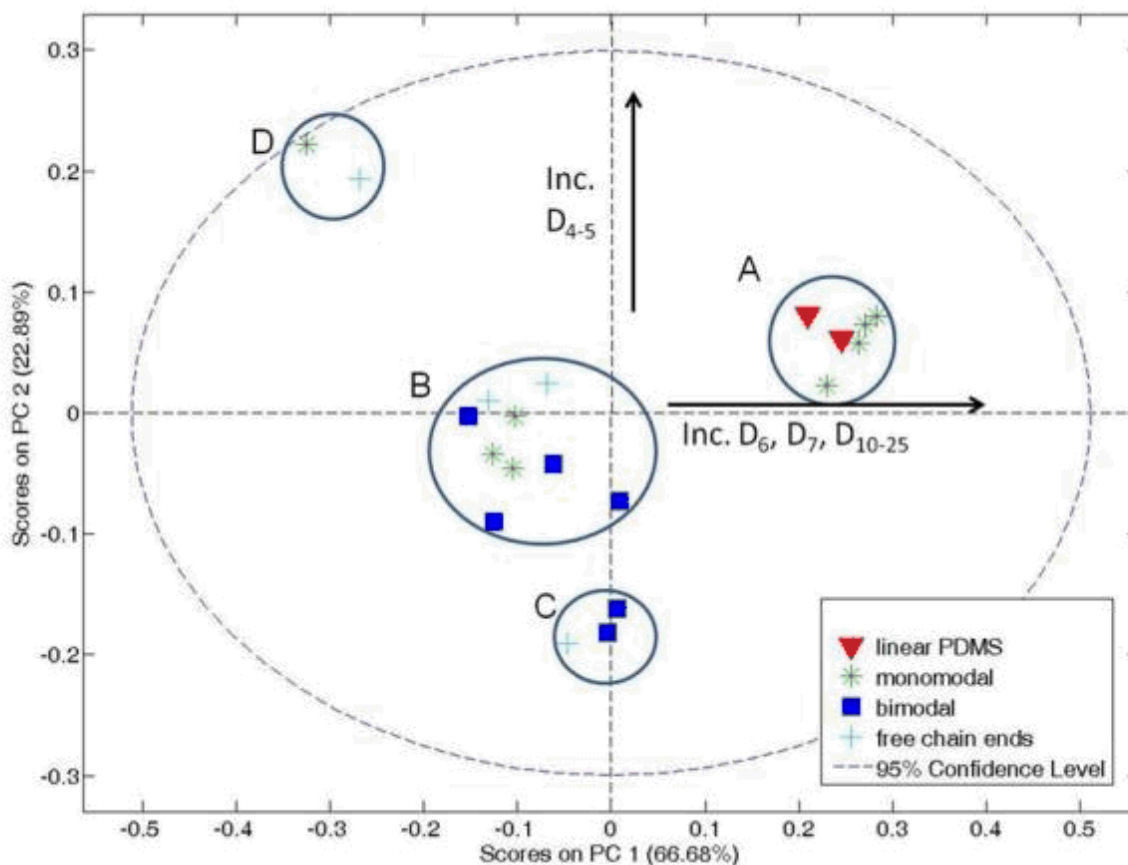
2) Lewicki JP, Liggat JJ and Patel M. *Polymer Degradation and Stability* 2009, 94, 1548-1557.

Quantifying Degradation Chemistry as a function of Network Architecture – *Analytical Pyrolysis of Model Networks*

The thermodynamic product of thermal degradation in PDMS is not sensitive to the subtleties of network architecture.

Using a statistical Analysis technique we can examine the relationship between network architecture and minor product formation

We observe clear clustering of degradation profiles as a function of network structure



Lewicki JP, Mayer, BP, Alviso CT, and Maxwell, RS." *Journal of Inorganic and Organometallic Polymers and Materials* (2012) 22:636–645).

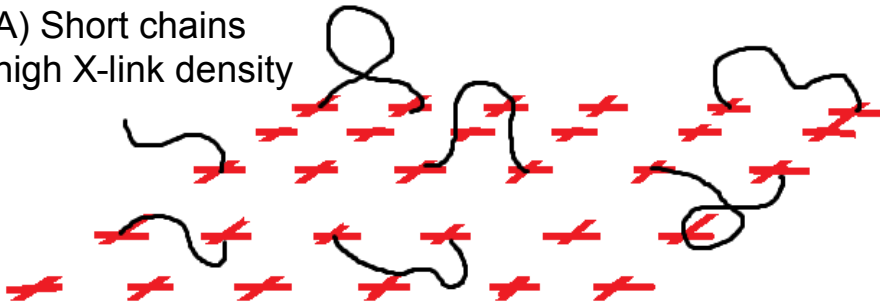
Quantifiable relationships exist between basic network architectures and the distributions of degradation derived species in PDMS networks.

Mechanistic Interpretation

Why are specific architectures altering the product profile?

- *Our analysis suggests that at shorter chain lengths/high x-link densities larger cyclics are favored. However at low x-link densities and long chain lengths smaller cyclics dominate*

A) Short chains
high X-link density



- **The additional constraint of high x-link density networks makes the formation of larger cyclics somewhat more conformationally favorable**



B) long chains
low X-link density

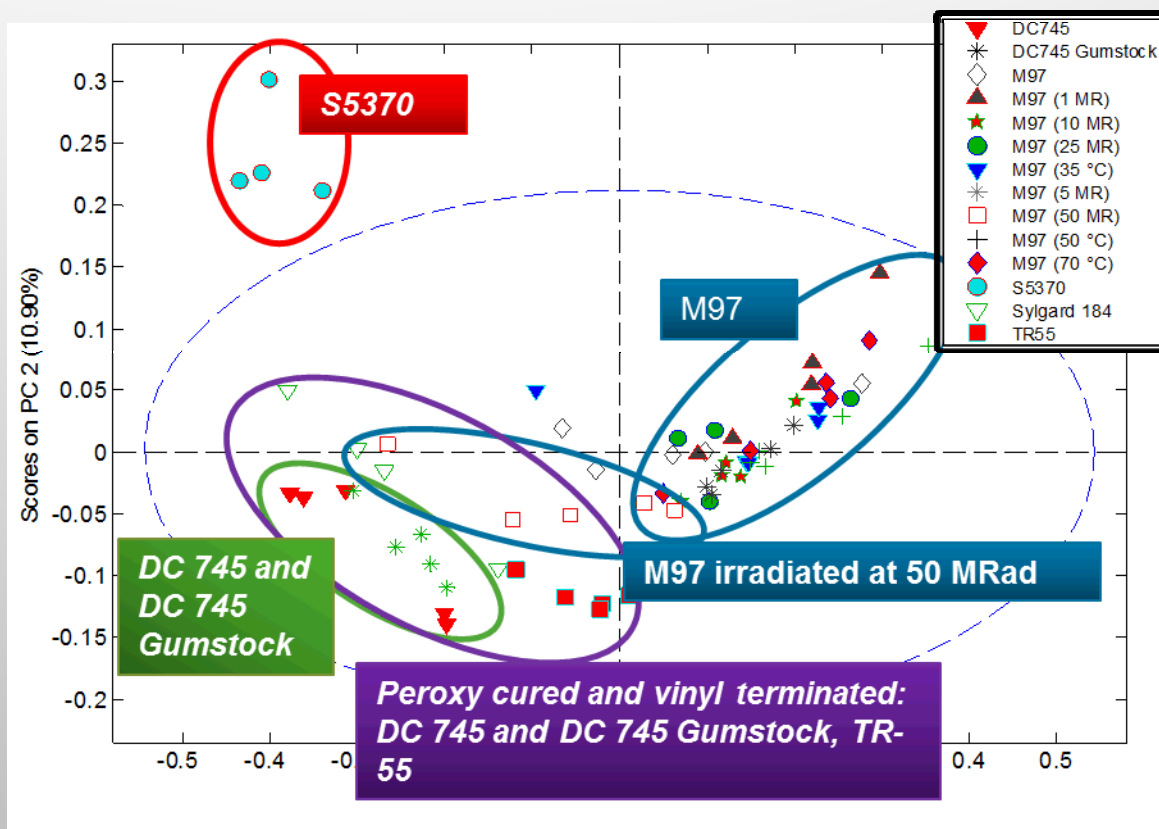


- **In low x-link density systems above entanglement random coil behavior dominates and the majority of a chain does not 'see' a x-link site, the main driver is now thermodynamics and small cyclic formation dominates**

Application to Engineering Silicones

Can we 'Fingerprint' real world materials as a function of degradation chemistry?

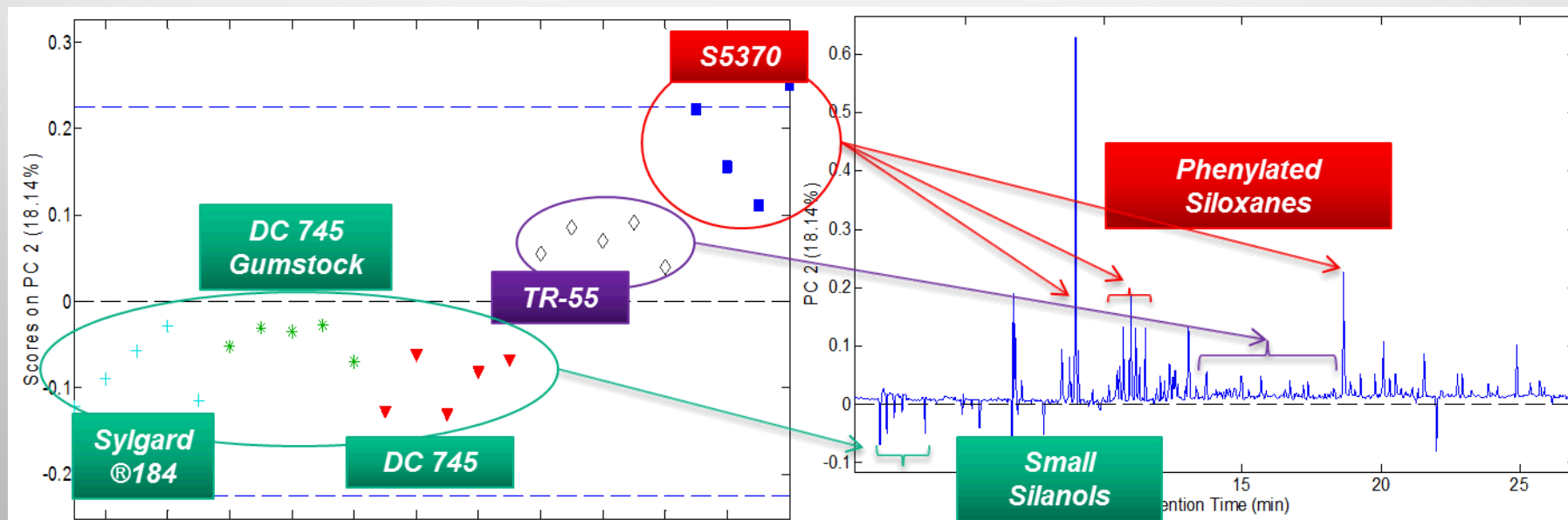
- Analytical pyrolysis coupled with PCA can map the degradation profiles of chemically similar engineering silicone elastomers
- Materials group by Network modality and catalyst chemistry
- Neither aging or irradiation significantly alter a materials pyrolysis degradation profile.



Lewicki, JP, Albo RLF, Alviso, CT and Maxwell, RS. "Pyrolysis-gas chromatography/mass spectrometry for the forensic fingerprinting of silicone engineering elastomers" *Journal of Analytical and Applied Pyrolysis* (accepted)

Application to Engineering Silicones

Global groupings are relatable to mechanistic changes arising from the materials unique network structure



- As with the model systems, architectural features such as phenyl free chain ends or high x-link densities 'skew' the profile of minor degradation products providing a fingerprint

Lewicki, JP, Albo RLF, Alviso, CT and Maxwell, RS. "Pyrolysis-gas chromatography/mass spectrometry for the forensic fingerprinting of silicone engineering elastomers" *Journal of Analytical and Applied Pyrolysis* (accepted, in press)

In summary

- The synthesis of well defined end-linked model PDMS networks allows us to decouple and investigate the effects of individual architectural motifs on the properties of a elastomer system
- X-link density, chain length, modality and level of FCE's all influence the degradation chemistry of a silicone material
- Here we have demonstrated the utility of interrogative thermal analytical analysis methodologies for the study of otherwise intractable materials

- Thank you.

Questions?

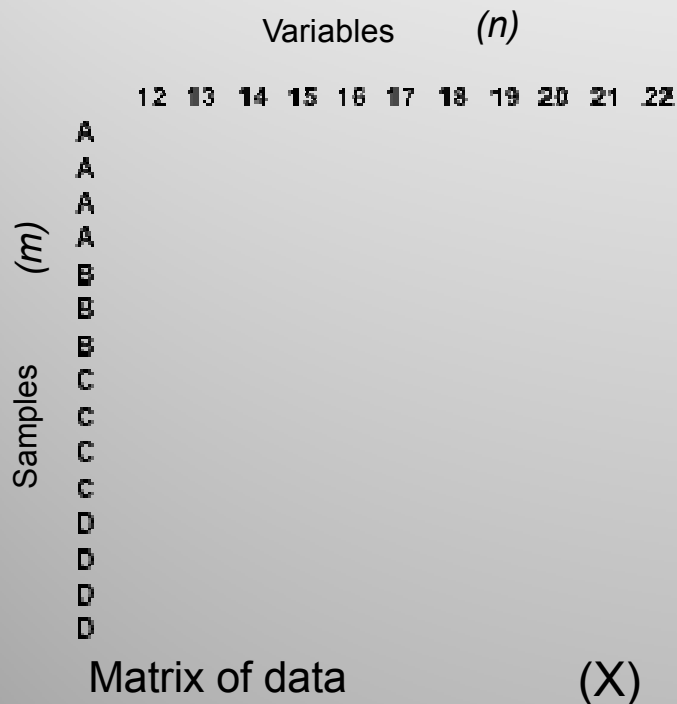
Backups

Multivariate Statistical Analysis

COMPLEX = scale, similarity, etc.

Examples of variables (n): *Pressure, temperature, absorbance, intensity, etc.*

Examples of samples (m): *Data samples at specific time points, # of samples taken in a study.*



Principle
component
analysis

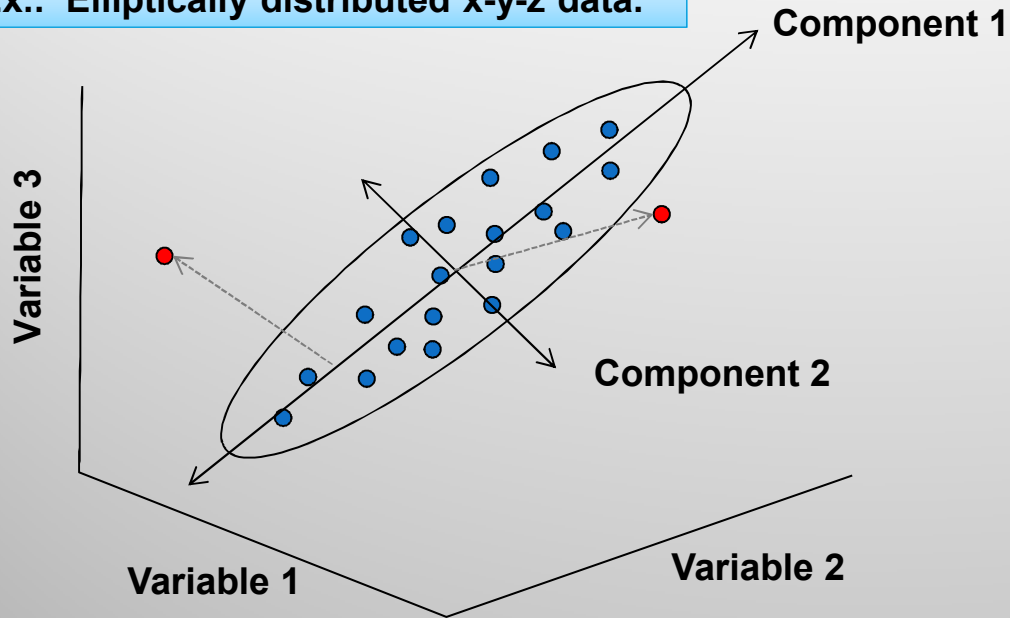
Small number of new variables or **“components”** that maintain structure of the data (i.e., the basic information) but that can **better capture the data’s variance**.

These components give information on:

- How samples are (or aren’t) related to one another
- The degree to which variables influence the overall structure of the data.

The key is dimensional reduction

Ex.: Elliptically distributed x-y-z data.



PCA can also identify outliers and discriminate between outliers within the model and outside the model.

Principle Component 1:

- Accounts for the largest variance (spread) in the data.

Principle Component 2:

- Orthogonal to PC1, accounts for next largest variance.

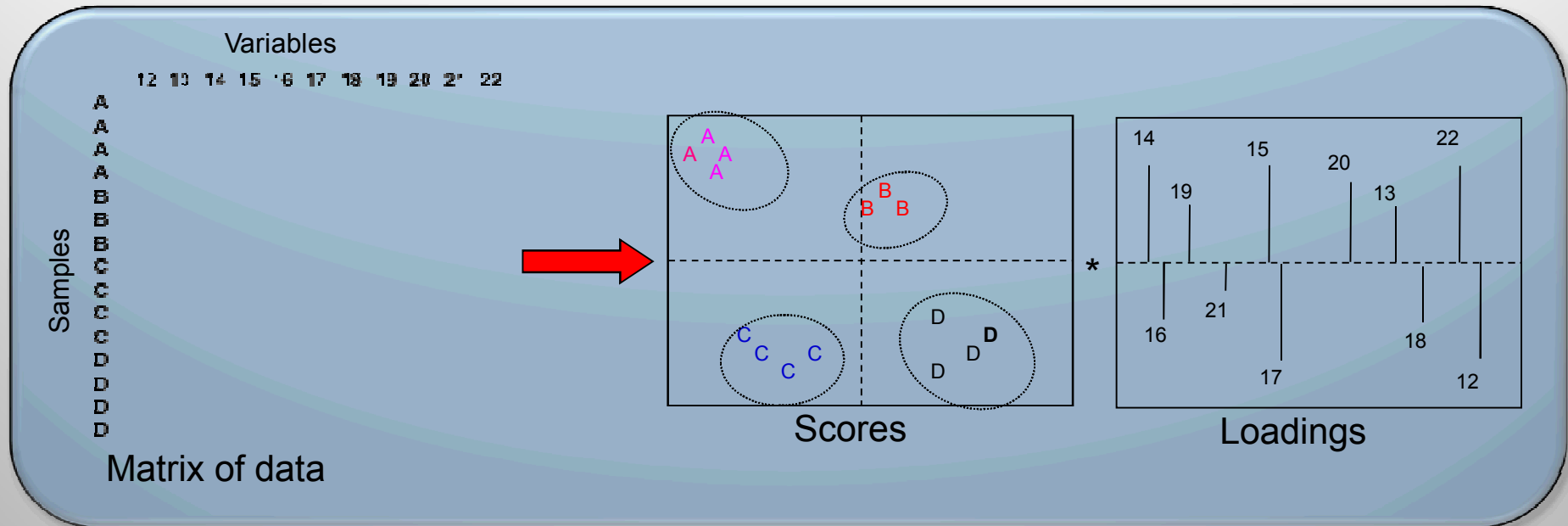
Principle Component 3:

- Direction forced by # of variables (3)
- Not necessary!!! – little variance in last remaining new dimension

Dimension Reduction by discarding unnecessary components...

- ...unimportant 'variables'
- ...spectral noise
- ...etc.

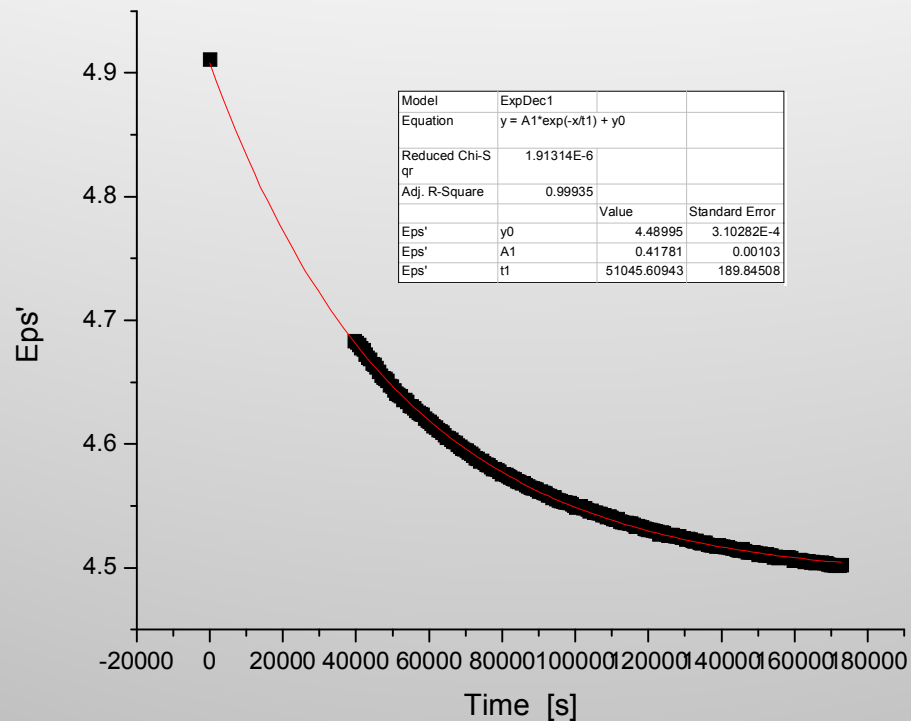
We can then examine the relevant variation in the data in straightforward manner



Scores describe the relationship of the samples – how the samples group to (or separate from) each other.

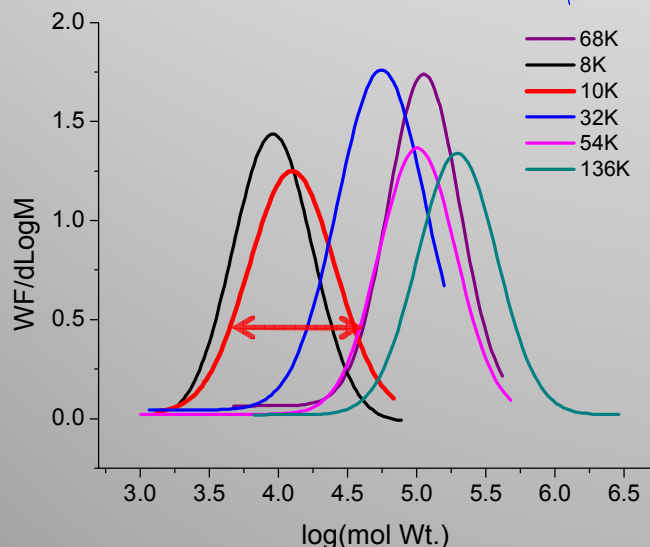
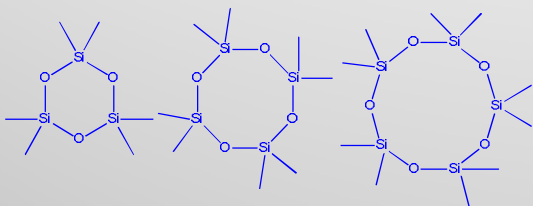
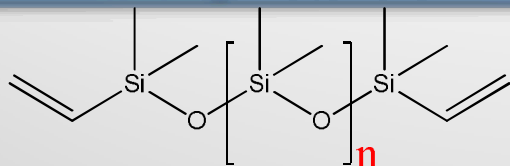
Loadings identify the variables that contribute to the grouping and/or separation.

BDS measurement of PDMS cure in real time

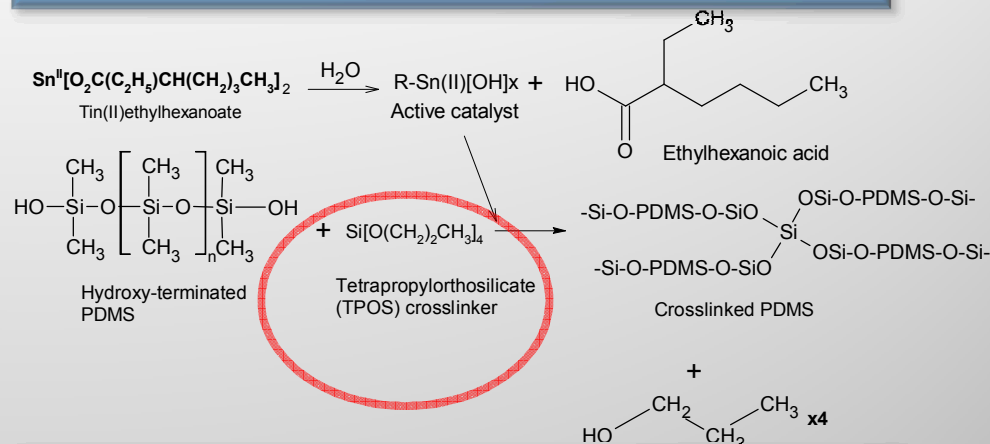


Practical Considerations – Obtaining a network structure that is close to ‘ideal’ can be challenging

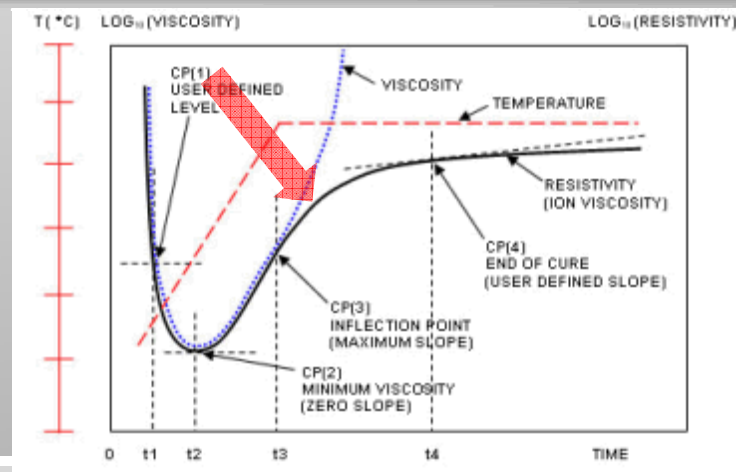
Purity & polydispersity of the starting materials



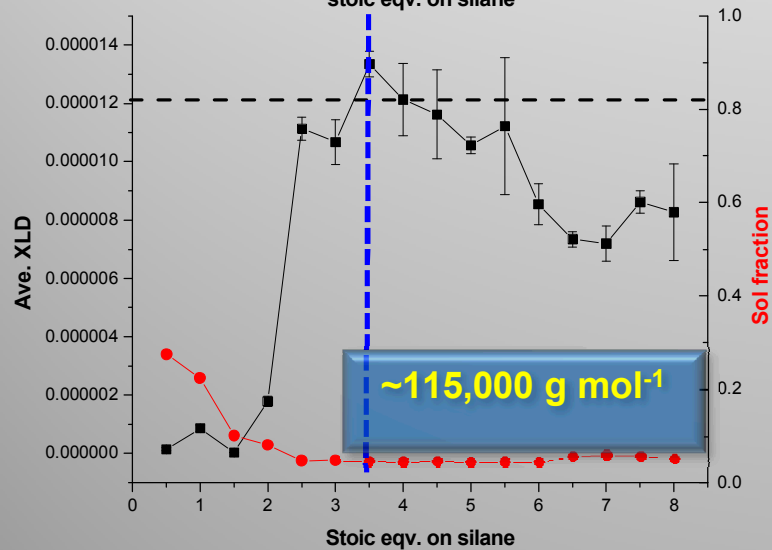
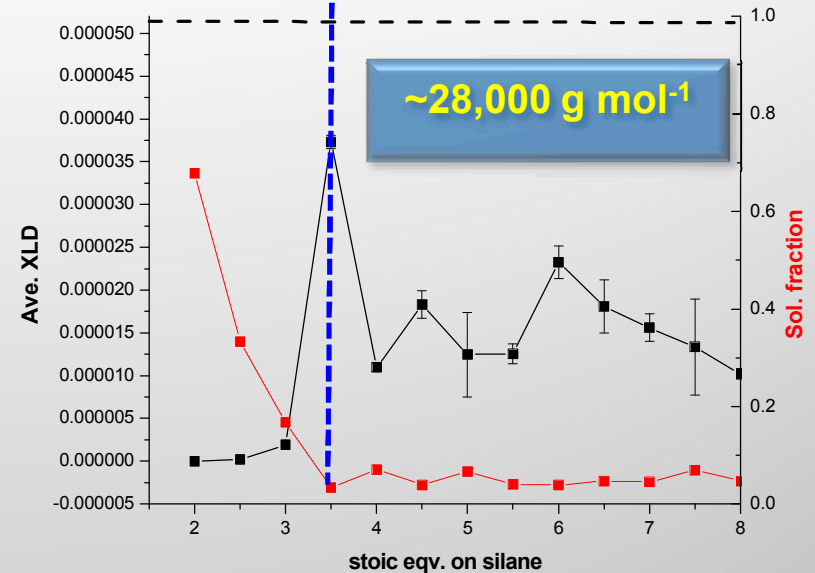
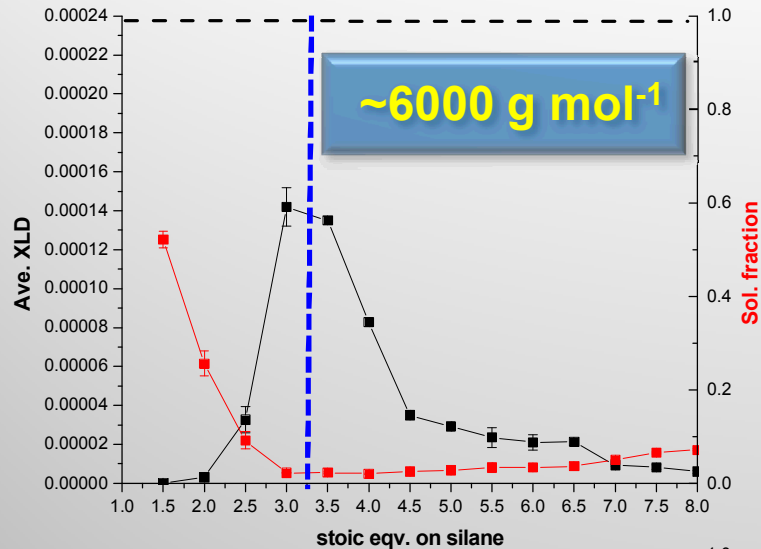
Unwanted side reactions



Complex cure kinetics



Optimizing Model Networks - Equilibrium solvent uptake measurements provide a measure of x-link density and residual sol. fraction

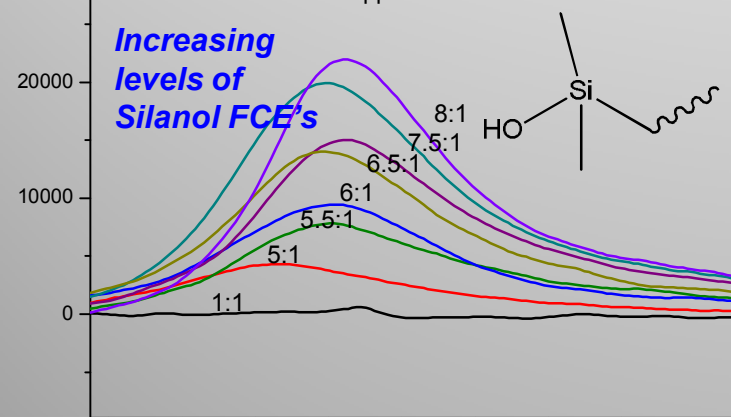
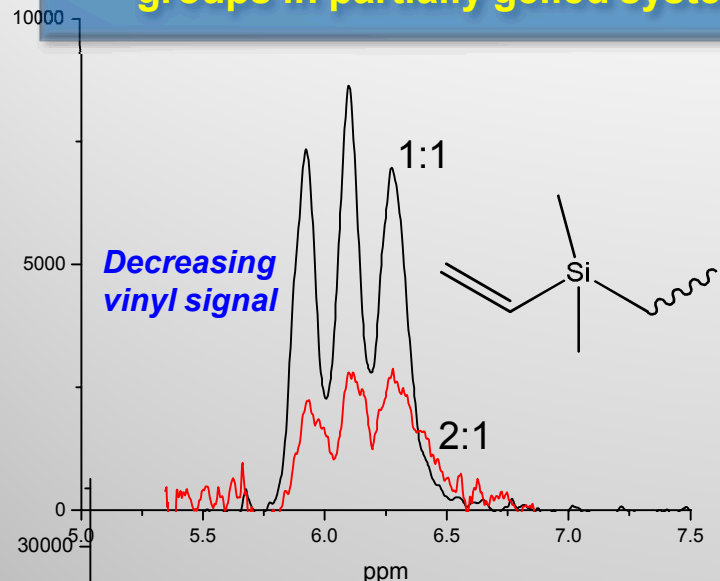


- Assessment of crosslink density with the application of F-H network theory.

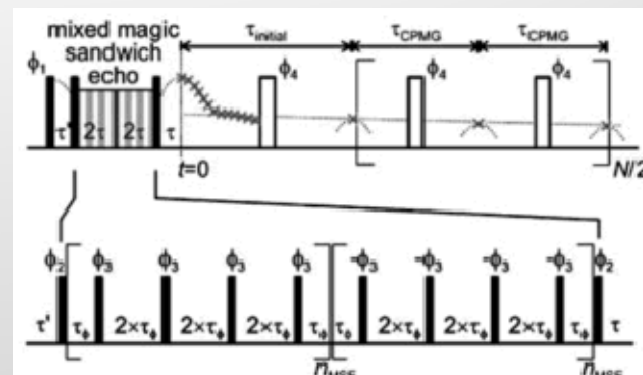
$$\langle M_x \rangle = \frac{-\rho_{poly} V_{m,solv} (c^{1/3} - \frac{c}{2})}{[\ln(1 - c) + c + \chi c^2]}$$

Spectroscopic Methods for Assessing Network Ideality – Solid State ^1H NMR

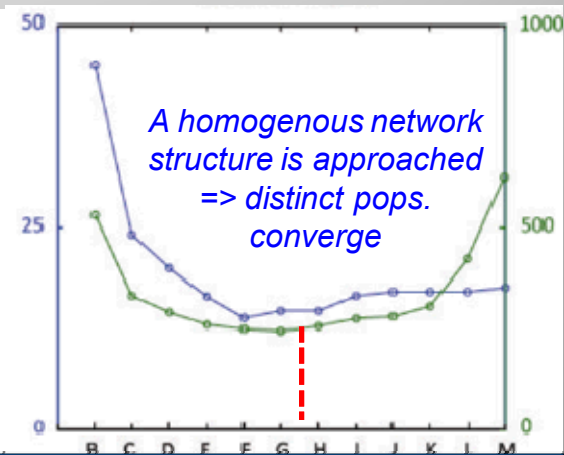
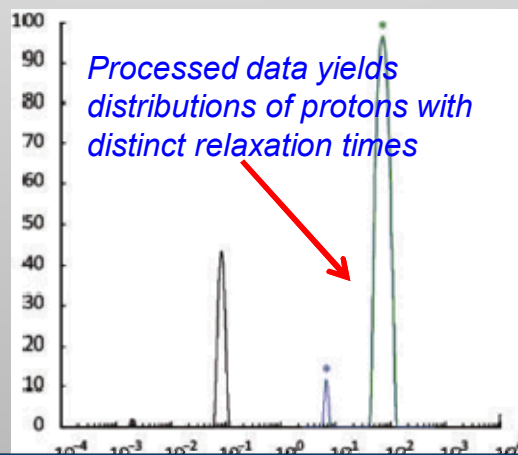
- ^1H MAS – Can directly observe the excesses of functional groups in partially gelled systems



- Magic Sandwich Echo allows protons associated with regions of differing mobility to be assessed

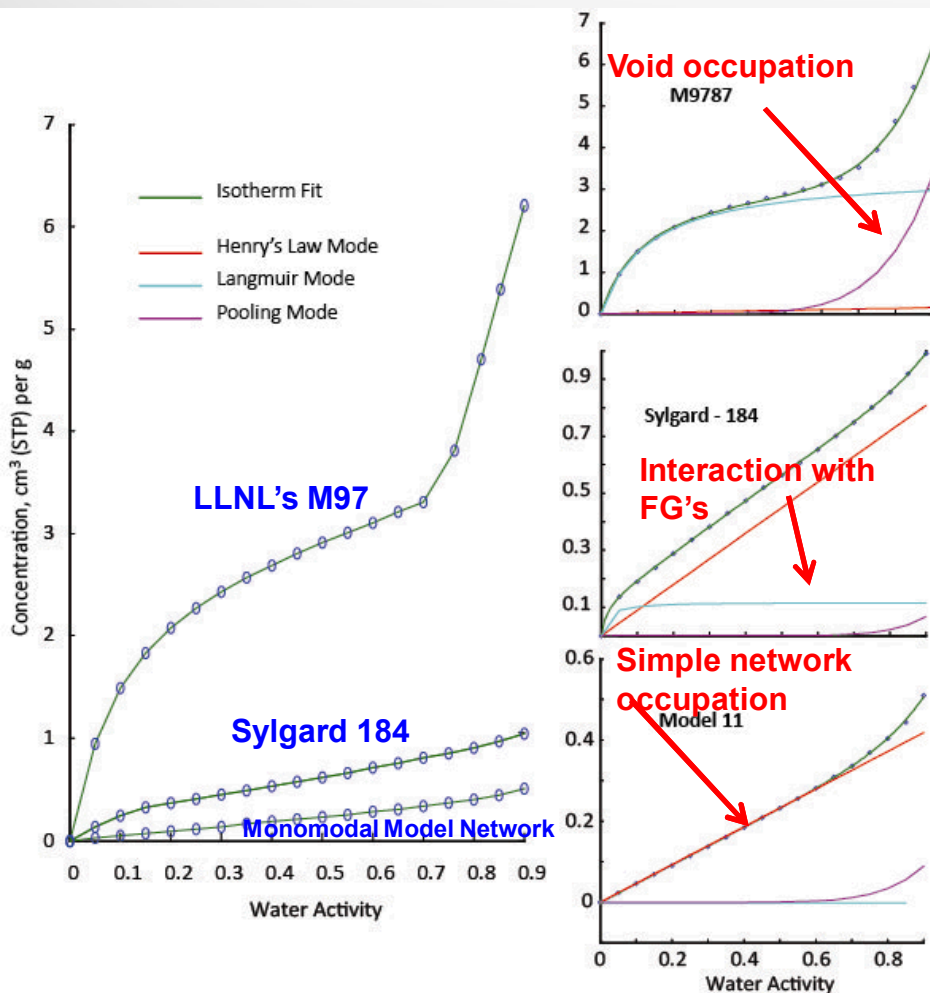


Maus et. al Macro. Chem. Phys. 207, 13, 2006



- The progress of a structure towards a homogenous, ordered network can therefore be followed using convenient, non-invasive and easy to implement solid state NMR methodologies

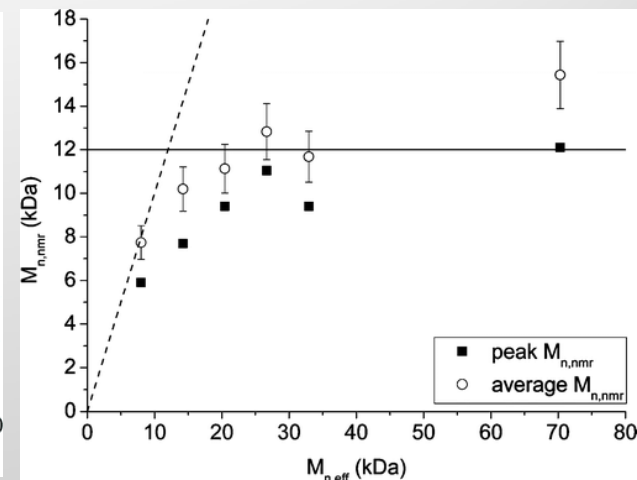
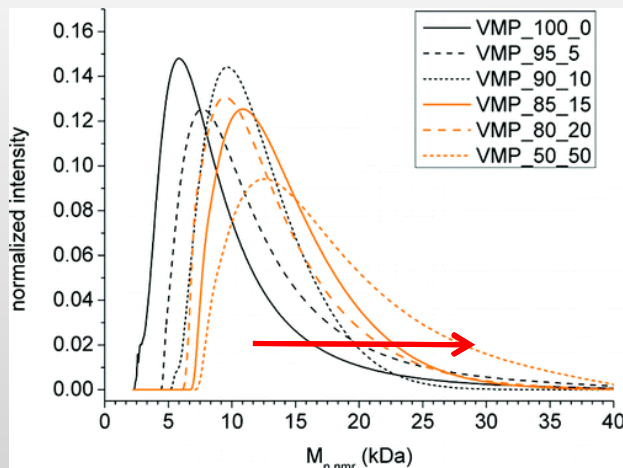
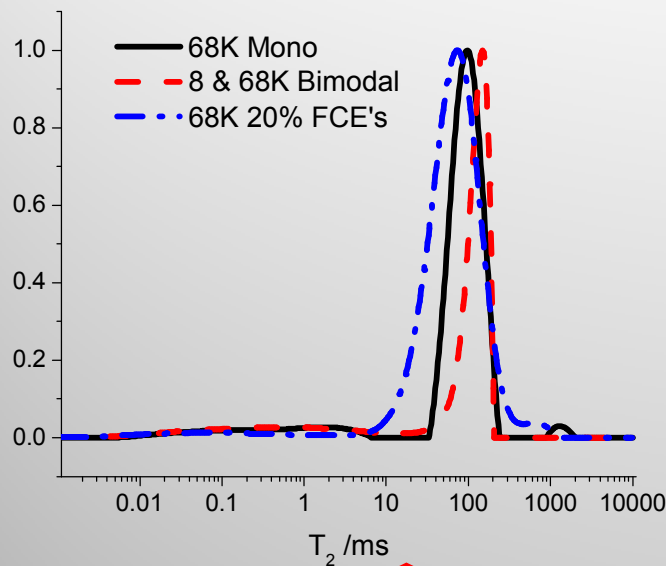
Model Behavior – Characterization tools for investigating polymer physics



Water sorption studies yield insight into the dynamics of siloxane networks

- In contrast to commercial and end-use formulations, the uptake behavior of the optimized model systems is linear and single component.
- Residual functionality and void volume in Sylgard-184 and the LLNL end-use formulation (M97) lead to significant Langmuir and pooling sorption modes – absent in the model system.
- In the single component Henry's law behavior of the model network, we are observing the fundamental sorption behavior of the fully dense network

Reverse Engineering – Using well defined model networks as our yard-stick can we develop methodologies to back out structural information in the solid state?



Mayer, Lewicki, Weisgraber et al. MACROMOLECULES 44 8106 2011

Basic T_2 measurements have been shown to be sensitive network changes in the solid state

Multiple quantum NMR yield NMR derived distributions of MW through $\langle DQ \rangle$ - the residual dipolar coupling constant. MQ NMR is also sensitive to chain entanglements and M_c

Solid state NMR can be tasked as a powerful tool for the analysis of otherwise intractable polymeric network materials